

[Second Edition.]

PATENT SPECIFICATION

312,345

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COMPLETE SPECIFICATION.



Improvements in Catalytic Dehydrogenation.

We, E. I. DU PONT DE NEMOURS AND Co., a corporation organized and existing under the laws of the State of Delaware, United States of America, located at
5 Wilmington, New Castle County, State of Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates in general to catalytic dehydrogenation processes, more particularly to such processes for the converting of aliphatic primary alcohols to the corresponding esters, and specifically to such processes for the converting of ethyl alcohol to ethyl acetate. A major object of the invention is to improve upon such processes and, in particular, to provide processes of the general type wherein improved catalysts are utilized. To this end, and also to improve generally upon processes of the general character indicated, the invention consists in the various matters hereinafter described and claimed.

We are aware that it has been proposed to effect hydrogenations and dehydrogenations of carbon compounds while employing a catalytic agent comprising a metal such as iron, nickel, cobalt or copper with a difficultly reducible oxide such as the oxides of magnesium and manganese as promoters, the reaction to be carried out either at ordinary pressure or under increased pressure and which in most cases proceeds sufficiently rapidly at temperatures considerably below 180° C.

The present invention is directed particularly to the problem of converting primary alcohols into their corresponding esters and in accordance with the invention the improved process of converting a primary alcohol into its corresponding ester and other valuable products comprises passing the alcohol in the form of vapour and at an elevated temperature and pressure over a catalyst comprising copper and a difficultly reducible oxide or oxides.

In general accordance with the invention there is used a promoted catalyst [Price 1/-]

comprising copper and a promoting agent or agents, the agent being a difficultly reducible, i.e. substantially non-reducible dehydrogenating oxide, preferably of the second group of the Periodic table. In specific accordance with the invention the promoting agent may desirably be magnesium oxide. If desired more than a single oxide may be used, any two or more within the general concept of the invention being used, as magnesium oxide and zinc oxide, or magnesium oxide and manganese oxide. By substantially non-reducible oxides we mean those metallic oxides which are not essentially reduced to metal by prolonged exposure in a state of purity to the action of hydrogen at atmospheric pressure and 400° C. to 450° C.

We are aware that copper, prepared by the reduction of its oxide, has long been known as a catalyst for the dehydrogenation of alcohols. It is further known particularly from the investigations of Palmer in England Proc. Roy. Soc. 101 A, 175 (1922), that certain non-reducible metallic oxides greatly enhance the activity of copper in the dehydrogenation of alcohols at atmospheric pressures. Also, we are aware that it has been proposed to use promoted copper catalysts for the high pressure synthesis of methanol from gases containing carbon monoxide and hydrogen. We make claim to none of these features.

The invention finds particularly valuable application in those dehydrogenation processes for the direct synthesis of esters from alcohols, particularly the production of ethyl acetate and other valuable products from ethanol under high pressure. Such a process may, in brief, be as follows:—Ethyl alcohol is pumped into a boiling vessel maintained at a temperature above the critical temperature of the alcohol, e.g. 300° C., where it is converted to a vapor; the vapor is conducted over a catalyst (e.g. copper oxide) in a pressure resisting tube maintained at 350° C., at a rate equal to four volumes of liquid ethyl alcohol for each volume of catalyst per hour, and the effluent gases are passed under pressure to a condensing coil

Price 4s 6d

where there separates unchanged alcohol containing in solution ethyl acetate, etc., the uncondensed hydrogen is bled out of the system at such a rate as to maintain the pressure in the system at 275 atmospheres.

On account of the adverse effect that should theoretically result from the application of high pressure to dehydrogenation processes, it was not to be expected that valuable results could be obtained with promoted copper catalysts; but the fact is, we have found, that with practice in accordance with the present invention, highly valuable results are obtained. The effect of the promoter is two-fold; it brings about a greater initial production than that given by pure copper under similar conditions, and it increases the period of high activity by causing a delay in the onset of the catalyst deterioration.

In illustration of the above, we give, by way of example merely:—

EXAMPLE 1.

An oxide composition is prepared by melting by means of an electric current a mixture of about 1 part by weight of magnesium oxide, about 4 parts by weight of zinc oxide and about 20 parts by weight of pure cupric oxide. The mass is cooled, crushed and screened to a convenient grain size, after which it is slowly reduced at 150° C. in a gas mixture consisting of about 80% carbon dioxide and 20% hydrogen. The vapor of 95% ethanol, which should be reasonably free from catalyst poisons, such as hydrogen sulphide, is passed over the catalyst at a rate equal to about four volumes of liquid ethanol for each volume of the catalyst per hour at a temperature of 375° C. and pressure of 4000 lbs. per square inch. The condensed liquid products consist of unchanged ethanol containing about 20 percent by weight of ethyl acetate, about 5% by weight of normal butanol and other higher products, and about 1.5% by weight each of acetaldehyde and acetic acid. After about 40 hours of continuous operation, the yield of ethyl acetate is diminished by less than 20%. (As illustrating the improvement due to the promoter, a similarly prepared pure copper catalyst yields under the same conditions a condensate containing only 6 percent by weight of ethyl acetate, which after 12 hours of use has dropped to about 4 percent.)

EXAMPLE 2.

A copper catalyst prepared according to the method described in Example 1, but containing 2.0% by weight of magnesium oxide as the promoter when used for the production of ethyl acetate under

the conditions described in Example 1, yields a condensate containing about 16% by weight of ethyl acetate and about 10% of other liquid products including acetaldehyde, acetic acid, acetone, and normal butanol.

EXAMPLE 3.

Fuse 1 kilogram of pure cupric oxide and dissolve in the melted oxide a mixture of 75 grams of manganese oxide and 25 grams of magnesium oxide. Cool the homogeneous mass and crush it to small granules. Reduce the granules by passing over them the vapors of ethanol at a temperature 225-250° and at atmospheric pressure. When used according to Example 1, this catalyst converts about 16.5, 2.0, 1.8, 7.5 and 4% by weight of the ethanol to ethyl acetate, acetaldehyde, acetic acid and hydrocarbons, respectively.

Returning now to the substantially non-reducible oxides utilized in accordance with the present invention, a large number of these, when employed singly as promoters for copper, are found to enhance the initial production of esters, among which are the alkali earth oxides of the second group of the Periodic Table; also the non-reducible oxides of the other sub-group of the same group, including zinc oxide and magnesium oxide. We may also elect to employ manganese oxide, an oxide of the acidic type such as chromium oxide, or one or more oxides of the rare earth group. Non-reducible metallic oxides have been classified by Sabatier (Catalysis in Organic Chemistry) as dehydrating, dehydrogenating and mixed. We have found most suitable as promoters those oxides which are predominantly dehydrogenating in their action on alcohols. We wish particularly to emphasize the value of magnesium oxide, either when employed alone or together with another of the oxides named. An especially good result is obtained when magnesium oxide is employed in a copper catalyst together with one of the predominantly dehydrogenating oxides, namely, zinc oxide or manganese oxide. The relative proportion of the two promoter oxides may be varied considerably, but we prefer to use about two molecular weights of the zinc oxide or manganese oxide for each molecular weight of magnesium oxide. For example, a suitable catalyst for the production of ethyl acetate from ethanol may consist of 15 moles of manganese oxide, 8 moles of magnesium oxide, and 77 moles of copper. The manganese oxide may be replaced wholly or in part with zinc oxide with a similar result.

The kind or amount of oxide promoter has little effect on the distribution of

- liquid products other than esters, for example, higher alcohols, aldehydes, acids or ketones, or on the composition of the gas. However, we prefer not to employ an oxide promoter whose catalytic nature is predominantly dehydrating, alumina being such an oxide, for then the undesirable side reaction of dehydration is apt to be magnified. If such a dehydration reaction does take place in the presence of a copper catalyst, the olefinic hydrocarbon produced is, for the most part, hydrogenated to the corresponding saturated hydrocarbon and is lost to useful purposes. Although it is not imperative, we also prefer to exclude from the catalyst metals of the iron and platinum group since these metals are active for the destruction of alcohols to gaseous products such as methane, carbon monoxide, and carbon dioxide.
- A convenient method of preparing promoted copper catalysts consists of fusing a mixture of pure copper oxide with one or more non-reducible metallic oxides, after which the melt is crushed and reduced with hydrogen, carbon monoxide, or alcohol vapor. The fusion may be carried out by a resistance furnace by use of a gas torch, or by any other suitable means. Although we prefer to start with cupric oxide, oxygen is lost during the fusion process, leaving a finished product largely in the cuprous oxide state. The upper limit of the amount of promoter constituents that may be added is determined by the extent of elevation of the melting point and increase in viscosity of the melted copper oxide mixture. In general, we prefer to use not less than 2 nor more than 85 molecules of promoter per 100 molecules of cupric oxide. In place of using the non-reducible metallic oxides, we may employ instead the hydroxides, carbonates, oxalates, or other salts or compounds which yield the oxides under the conditions of the fusion process.
- Great care must be exercised in the reduction of these highly active catalysts. With pure hydrogen the reaction is so vigorous as to cause a rapid temperature rise resulting in seriously impairing the activity of the catalyst. Satisfactory results have been obtained by reducing the melted oxides in a mixture of hydrogen and an inert gas such as carbon dioxide or nitrogen at 150°. A more rapid method consists of reducing in the vapor of ethanol at 225–250°.
- Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—
1. An improved process of converting primary alcohols into their corresponding esters and other valuable products which comprises passing an alcohol in the form of a vapour and at an elevated temperature and pressure over a catalyst comprising copper and a difficultly reducible oxide or oxides.
 2. An improved process as claimed in Claim 1 in which the reactant is a primary aliphatic alcohol.
 3. An improved process as claimed in Claim 2 in which ethyl alcohol is the reactant.
 4. An improved process as claimed in any of the preceding claims in which the difficultly reducible oxide or oxides is an oxide of a metal of the second group of the Periodic Table.
 5. An improved process as claimed in Claim 4 in which the catalyst comprises magnesium oxide and manganese oxide.
 6. An improved process as claimed in Claim 5 in which the manganese oxide is replaced wholly or in part with zinc oxide.
 7. An improved process as claimed in Claims 5 and 6 in which the relative proportions of the difficultly reducible oxides in the catalyst is about two molecular weights of zinc oxide and/or manganese oxide for each molecular weight of magnesium oxide.
 8. An improved process as claimed in Claim 7 in which the catalyst comprises 15 moles of manganese oxide and/or zinc oxide, 8 moles of magnesium oxide and 77 moles of copper.
 9. An improved process as claimed in any one of the preceding claims in which the catalyst is prepared from a mixture containing cupric oxide preferably containing not less than 2 nor more than 85 molecules of difficultly reducible oxides per 100 molecules of cupric oxide, said mixture being reduced to form free copper.
 10. An improved process as claimed in Claim 9 in which the catalyst employed is formed by the reduction of a cupric oxide containing mixture at a temperature of 150° C. in an atmosphere of hydrogen and an inert gas such as carbon dioxide or nitrogen.
 11. An improved process as claimed in Claim 10 in which the catalyst employed is prepared by melting a mixture of about 1 part by weight of magnesium oxide and about 4 parts by weight of zinc oxide and about 20 parts by weight of pure cupric oxide, subsequently cooling, crushing and screening the mass to a convenient grain size and thereafter slowly reducing the mass at 150° C. in a gas mixture consisting of about 80% carbon dioxide and 20% hydrogen.
 12. An improved process as claimed in Claims 1 to 11, in which ethyl alcohol is

passed in contact with a catalyst, comprising copper and magnesium oxide at a temperature of at least 375° C. and at a pressure of about 4000 pounds per square inch.

5 18. The improved process of converting a primary alcohol into its corresponding ester substantially as hereinbefore described.

Dated this 8rd day of April, 1929.

MARKS & CLERK.

Reference has been directed in pursuance of Section 7, Sub-section 4 of the Patents and Designs Acts 1907 to 1928, to Specification No. 287,846.

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